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SURFACE ZnSe:Ca LAYERS WITH HOLE CONDUCTIVITY

The authors investigate the effect of treating n-ZnSe substrates with boiling aqueous $\text{Ca}(\text{NO}_3)_2$ suspension on their electrical and luminescent properties. Base substrates were cut from bulk pure zinc selenide crystals grown from a stoichiometric melt by the Bridgman method. It was found that the Ca-doping of the substrates causes an almost complete “quenching” of the low-energy orange emission band with a maximum near $\hbar\omega_{\max} \approx 1,95$ eV and a significant increase in the efficiency of the edge blue luminescence band.

Keywords: zinc selenide, p-type conductivity, ionization energy, concentration, luminescence.

Despite the fact that zinc selenide has all the necessary physical and technological parameters for creating devices and instruments for short-wave electronics, this material still remains outside the scope of mainstream research. The main reason for this is that obtaining crystals and (or) layers with hole conductivity and preferential edge luminescence in the room temperature range is technologically difficult [1]. This is due to the large number of intrinsic and uncontrollable impurity defects, as well as the tendency of II–VI compounds to self-compensate, which ultimately leads to preferential electron conductivity of ZnSe [2]. Moreover, a theoretical analysis of the defect formation mechanisms in cadmium and zinc sulfoselenides allowed the authors of [3] to determine the temperature value (700 K), above which it is impossible to obtain impurity hole conductivity in these materials using traditional equilibrium methods. In such a case, therefore, p-type layers must be created by lower-temperature nonequilibrium methods — laser annealing, ion implantation, annealing in activated chalcogen vapors (or a combination thereof) [2]. A significant breakthrough in obtaining p-ZnSe was made by the authors of [4, 5], who suggested doping ZnSe layers created by molecular-beam epitaxy with nitrogen, activated by a radio-frequency discharge. It is this technology that made it possible to create the first blue-green laser structures based on II–VI compounds [6].

Further studies have shown that the efficiency of doping with the desired type of impurity (ac-

ceptor or donor) can be significantly improved by the simultaneous introduction of an opposite type of impurity [7, 8]. On the other hand, the end result of this co-doping is difficult to predict, since the complex process of defect formation depends on many factors, i.e., the technology for producing the base material and the ensemble of point defects, the method and mode of introducing compensating impurities, as well as their type and combinations. etc. In this regard, all the methods discussed above are far from simple, hard to predict theoretically, require complex and expensive equipment, as well as extra annealing of defects created due to the exposure to laser or ion fluxes.

With this in mind, doping these compounds with isovalent impurities (IVIs) exhibiting a significantly different behavior from that of typical donor and acceptor impurities [4, 5, 9] may be promising. One of the features of an IVI is that it generates its intrinsic point defects (IPD) of a certain type, not always creating their own local levels in the forbidden zone of the semiconductor. The type of IPD (donor or acceptor) determined by the electronegativity factor X_{IVI} and the atom of a semiconductor compound replacing it, and the concentration of the resulting IPD can be commensurate with the concentration of the introduced IVI [6]. Using the results of [5, 6], we can conclude that inequation $X_{\text{IVI}} < X_{\text{Zn}}$ must be fulfilled to generate self-defective acceptor centers. This condition is true for a number of elements from group II of the periodic table (Be, Mg, Ca, Ba), whose integration into the cationic (zinc) ZnSe sublattice

stimulates the appearance of additional zinc vacancies V_{Zn} and interstitial selenium Se_i . Our choice of calcium as an IVI is based on the fact that the difference in the electronegativities of Ca and Zn are fairly strong [5], and the solubility of calcium salts in water is the highest compared to similar salts of the other elements mentioned above [10].

Another feature of the IVI is an increase in the edge radiation efficiency, whether the energy zone structure is direct or indirect [11, 12]. This effect, in particular, is observed experimentally in single-crystal CdTe and ZnSe substrates doped with group II elements with magnesium and calcium [7, 15]. Note that, regardless of the type of IVI used (Mg and Ca) and the method of its introduction (vapor phase or solution), the luminescence spectra is dominated by the edge emission band at a doped substrates temperature of 300 K. In our opinion, the conclusions the authors of these works made about the hole conductivity of the obtained layers was not sufficiently substantiated.

Thus, in this study, we analyzed the electro-physical properties of the ZnSe:Ca diffusion layers, using the above-considered mechanisms for the formation of acceptor centers and the determination of their main parameters.

Samples and research methods

The substrates were 4×4×1 mm plates cut from a bulk ZnSe crystal grown from a stoichiometric composition melt. In the room temperature range,

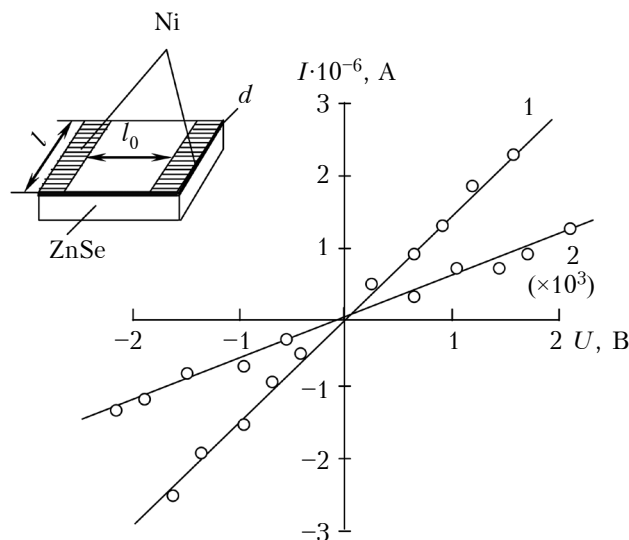


Fig. 1. $I - V$ characteristics of the ZnSe:Ca layer with Ni contacts (1) and the substrate with In contacts (2) obtained at 300 K (insert presents a schematic drawing of the substrate after annealing)

the substrates had a weak electronic conductivity of $\sigma_p \approx 10^{-9} \Omega^{-1} \cdot \text{cm}^{-1}$. Before doping, the plates underwent mechanical and chemical polishing in solution $\text{CrO}_3:\text{HCl} = 2:3$, which gave their surface a mirror-like aspect. Doping was carried out by an hour-long annealing of the substrates in a boiling aqueous suspension of the $\text{Ca}(\text{NO}_3)_2$ salt. After that, their surface layers changed the electron conductivity to the hole one, which is confirmed by the signs of thermoelectric power and by the fact that the contact becomes rectifying. Then, Ni was sprayed onto one of the large sides of the plates in strips, which served as ohmic contacts (OC) to the final layer. A schematic representation of the substrates that have passed the stage of annealing and OC deposition is shown in Fig. 1 (see insert).

The linearity and symmetry of the current-voltage characteristics ($I - V$) shown in Fig. 1 of the Ni contacts confirms their resistivity and the hole conductivity of the obtained layers (for clarity, the values of the parameters of dependence 2 are multiplied by 10^3). At the same time, similar contacts to n -ZnSe substrates have non-linear $I - V$ characteristics, which indicates the presence of a potential barrier between nickel and zinc selenide layers. Meanwhile, the above experimental facts are not at all consistent with any of the metal-semiconductor contact models (Schottky or Bardeen) [16], which calls for additional research beyond the scope of this work. Fortunately, this does not prevent us from determining a number of parameters of the obtained layers, in particular, the ionization energy E_a and concentration N_a of electrically active acceptor centers. The former can be found from the temperature dependence of the specific conductivity.

Electronic conductivity σ_p or resistance ρ_p are related to the concentration p_0 and mobility μ_p of equilibrium holes by a simple ratio [17]

$$\sigma_p = 1 / \rho_p = e \mu_p p_0. \tag{1}$$

Note that the dependency $\sigma_p(T)$ is actually determined by the stronger dependence of the factors in (1) that vary with temperature according to the law [17]

$$\mu_p(T) \sim T^m; p_0 \sim T^{3/2} \exp(-E_a / (nkT)). \tag{2}$$

Here m changes from $-3/2$ to $3/2$ depending on the scattering mechanism, and $n=1$ or $n=2$ for a strongly or slightly compensated semiconductor. Note also that in our case it is much easier to

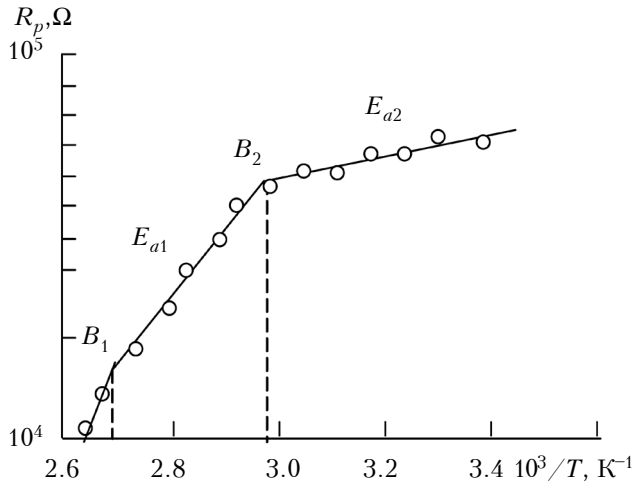


Fig. 2. Temperature dependence of the ZnSe:Ca diffusion layer resistance

measure the resistance of the layer R_p , which then allows you to easily calculate ρ_s (or σ_s) according to the formula

$$\rho_p = 1/\sigma_p = R_p s/l = R_p l_0 d/l, \quad (3)$$

l, d – length and thickness of the diffusion layer;
 l_0 – width of the Ni contact (see the insert in Fig. 1).

The correctness of this approach is due to the fact that the diffusion p -layer is isolated from the substrate by an n -ZnSe i -layer with the lowest possible conductivity, which electrically unites them. The ionization energy of electrically active centers in the p -layer can be found using expressions (1) and (2), assuming that $\sigma_p(T)$ is determined mainly by the exponential factor, i. e., actually by $p_0(T)$. This is confirmed by the data in **Fig. 2**, which shows that the experimental dependencies $R_p(T)$, plotted in coordinates $\ln R_p - 10^3/T$, are straight lines with the energy slope corresponding to the E_a slope. The calculated values of the activation energies with regard to the weakly compensated p -layer are given in **Table** and correlate with the depth of the acceptor levels of alkali metal impurities $E_a \approx 110 - 120$ meV and singly charged zinc vacancies V'_{Zn} from $E_a \approx 150 - 200$ meV [2, 17]. The uncontrolled alkali metal impurities are likely to be present in small quantities in the $\text{Ca}(\text{NO}_3)_2$ salt.

Using the parameters at the break points B_1 and B_2 on the curve of $R_p(T)$ dependence at which the Fermi level crosses the level of the corresponding center, we can determine the concentration of electrically active acceptor centers using the formula [17]

$$N_a = N_v \exp(-E_a / (kT_B)). \quad (4)$$

Effective density of state in the N_v valence band is easily calculated by the formula

$$N_v = 2(2\pi m_p^* kT / h^2)^{3/2}. \quad (5)$$

If we know that, for ZnSe, $m_p^* = 0,6m_0$ [2], we can calculate that $N_v \approx 8 \cdot 10^{19} \text{ cm}^{-3}$ (for 300 K). We can then find N_a , given its dependence on T and the corresponding E_a and T_B values (see Table 1). Due to the absence of a horizontal plot on the graph of the dependence $R_p(T)$ corresponding to the “depletion” of the acceptor center, the free holes concentration should be calculated by the formula

$$p_0 \approx \sqrt{N_v N_{a1} / 2} \cdot \exp(-E_{a1} / (2kT)). \quad (6)$$

Substituting the required values of N_v, N_{a1}, E_{a1} and $T = 300$ K into formula (6), we find that $p_0 \approx 8 \cdot 10^{17} \text{ cm}^{-3}$, which, given the hole mobility $\mu_p \approx 30 \text{ cm}^2/(\text{V}\cdot\text{s})$ [2], leads to the conductivity value $\sigma_p \approx 4 \text{ } \Omega^{-1}\cdot\text{cm}^{-1}$. The diffusion layer thickness is easy to find by substituting the experimental and calculated parameters l, l_0, R_p and σ_p into expression (3). For this sample, the diffusion layer thickness was determined to be approximately $0.15 \text{ } \mu\text{m}$.

In conclusion, we note that a sufficiently high hole conductivity of the obtained layers cannot be due to the new chemical compound formed as a result of treatment in the $\text{Ca}(\text{NO}_3)_2$ aqueous suspension. This is confirmed by a number of experimental facts. Firstly, the differential reflection spectra of the base and doped ZnSe substrates are identical, which indicates that their energy band structures are the same [15]. Secondly, there is a B band in the photoluminescence spectra of ZnSe:Ca layers, the shape and energy position of which are similar to the edge emission band of the base

The main parameters of p -ZnSe:Ca layers

Parameter	E_{a1} , meV	E_{a2} , meV	T_{B1} , K	T_{B2} , K	N_{a1} , cm^{-3}	N_{a2} , cm^{-3}	p_0 , cm^{-3}	d , μm
Value	110	200	320	380	$1,6 \cdot 10^{18}$	$3 \cdot 10^{17}$	$8 \cdot 10^{17}$	0,15

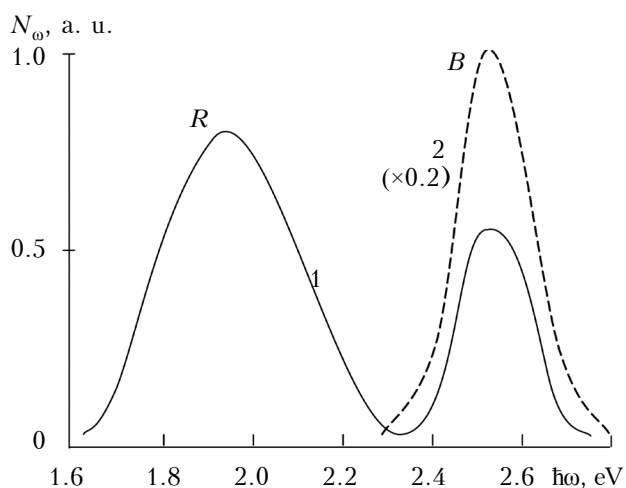


Fig. 3. Luminescence spectra of base (1) and Ca-doped (2) n -ZnSe substrates obtained at 300 K

substrates (Fig. 3, for clarity, the values of the parameters of dependence 2 are multiplied by 0.2).

Of particular practical interest is the fact that, in doped samples, the B -band is dominant, and its efficiency at 300 K is almost an order of magnitude greater than it is in base substrates (see Fig. 3). Therefore, we can assume that the observed transformation of the emission spectra is associated with the rearrangement of an ensemble of point defects in ZnSe, caused by the introduction of Ca impurity. We also draw attention to the fact that the exciting radiation of the N_2 -laser ($\lambda_m \approx 0,337 \mu\text{m}$) penetrates to a depth of less than $0.1 \mu\text{m}$, as a result of which it does not excite the luminescence in the base substrate and the observed emission spectrum is actually determined by the ZnSe:Ca layer diffusion (curve 2 in Fig. 3).

Conclusion

Thus, the research results convincingly indicate the possibility of creating p -type surface layers on n -ZnSe substrates by annealing them in a boiling aqueous suspension of $\text{Ca}(\text{NO}_3)_2$ salt. In this case, the conductivity is controlled by acceptor centers with activation energy values of 0.11 eV and 0.2 eV and estimated concentration of 10^{18} and $3 \cdot 10^{17} \text{ cm}^{-3}$, respectively. The presence of an effective edge emission band at 300 K in the luminescence spectra of ZnSe:Ca layers is also practically important. Further research, in our opinion, should be focused on studying the mechanisms of defect formation and luminescence, as well as directly determining the thickness of diffusion ZnSe:Ca layers and holes in them.

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ПОВЕРХНЕВІ ШАРИ ZnSe:Ca З ДІРКОВОЮ ПРОВІДНІСТЮ

Досліджено вплив обробки підкладок *n*-ZnSe в киплячій водній суспензії солі $\text{Ca}(\text{NO}_3)_2$ на їхні електричні та люмінесцентні властивості. Базові підкладки вирізались з об'ємних бездомішкових кристалів селеніду цинку, вироцених методом Бріджмена із розплаву стехіометричного складу. Встановлено, що обробка призводить до появи діркової провідності поверхневих шарів підкладок, величина якої за 300 К складає $\sigma_p \approx 4 \text{ Ом}^{-1}\cdot\text{см}^{-1}$. Значення енергії іонізації електрично активних акцепторних центрів, знайдені з температурної залежності опору R_p легуваного кальцієм шару селеніду цинку, дорівнюють $E_{a1} \approx 0,11 \text{ eV}$ та $E_{a2} \approx 0,2 \text{ eV}$. Значення їхніх концентрацій, розраховані з врахуванням характерних точок зламу на графіку залежності $R_p(T)$, складають для відповідних центрів $N_{a1} \approx 1,6 \cdot 10^{18} \text{ см}^{-3}$ та $N_{a2} \approx 3 \cdot 10^{17} \text{ см}^{-3}$. Оціночна концентрація вільних дірок в отриманих шарах за 300 К дорівнює $p_0 \approx 8 \cdot 10^{17} \text{ см}^{-3}$. Встановлено, що легування підкладок кальцієм викликає практично повне «гасіння» низькоенергетичної помаранчевої смуги випромінювання з максимумом поблизу $\hbar\omega_{\text{max}} \approx 1,95 \text{ eV}$ і значне збільшення ефективності крайової блакитної смуги люмінесценції.

Ключові слова: селенід цинку, діркова провідність, енергія іонізації, концентрація, люмінесценція.

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ПОВЕРХНОСТНЫЕ СЛОИ ZnSe:Ca С ДЫРОЧНОЙ ПРОВОДИМОСТЬЮ

Исследовано влияние обработки подложек *n*-ZnSe в кипящей водной суспензии соли $\text{Ca}(\text{NO}_3)_2$ на их электрические и люминесцентные свойства. Базовые подложки вырезались из объемных беспримесных кристаллов селенида цинка, выращенных методом Бриджмена из расплава стехиометрического состава. Установлено, что обработка приводит к появлению дырочной проводимости поверхностных слоев подложек, величина которой при 300 К составляет $\sigma_p \approx 4 \text{ Ом}^{-1}\cdot\text{см}^{-1}$. Значения энергии ионизации электрически активных акцепторных центров, найденные из температурной зависимости сопротивления R_p легированного кальцием слоя селенида цинка, равны $E_{a1} \approx 0,11 \text{ эВ}$ и $E_{a2} \approx 0,2 \text{ эВ}$. Значения их концентраций, рассчитанные с учетом характерных точек излома на зависимости $R_p(T)$, составляют для соответствующих центров $N_{a1} \approx 1,6 \cdot 10^{18} \text{ см}^{-3}$ и $N_{a2} \approx 3 \cdot 10^{17} \text{ см}^{-3}$. Оценочная концентрация свободных дырок в полученных слоях при 300 К равна $p_0 \approx 8 \cdot 10^{17} \text{ см}^{-3}$. Установлено, что легирование подложек кальцием вызывает практически полное «гашение» низкоэнергетической оранжевой полосы излучения с максимумом вблизи $\hbar\omega_{\text{max}} \approx 1,95 \text{ эВ}$ и значительное увеличение эффективности краевой голубой полосы люминесценции.

Ключевые слова: селенид цинка, дырочная проводимость, энергия ионизации, концентрация, люминесценция.

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